

TITLE

LITHIUM-SULFUR BATTERIES

CROSS REFERENCE TO RELATED APPLICATIONS

**[0001]** This application is based on Korean patent application Nos. 2000-44900 and 2000-44901 filed in the Korean Industrial Property Office on August 2, 2000, the disclosures of which are incorporated herein by reference.

BACKGROUND OF THE INVENTION

Field of the Invention

**[0002]** The present invention relates to a lithium-sulfur battery, and more specifically, to a lithium-sulfur battery exhibiting high capacity and good rate capability.

Description of the Related Art

**[0003]** A lithium-sulfur secondary battery uses sulfur-based compounds with a sulfur-sulfur bond as a positive active material, and a lithium metal or carbon based compounds as a negative active material. The carbon-based compounds in which intercalation chemistry occurs, include graphite, graphite intercalation compounds, and carbonaceous materials, where the carbonaceous materials are inserted with the lithium. Upon discharge (electrochemical reduction), a sulfur-sulfur bond is broken and results in a decrease in the oxidation number of S. Upon recharging (electrochemical oxidation), a sulfur-sulfur bond is formed and leads to an increase in the oxidation number of S.

**[0004]** The organic compounds which are able to dissolve the polysulfide that is the reduction products of the positive active materials are used as electrolyte solvents in the above lithium-sulfur battery. The choice of electrolyte solvents is important to the lithium-sulfur battery performance.

**[0005]** U.S. Patent Nos. 5,523,179 (PolyPlus Battery Company, Inc.), 5,532,077 (PolyPlus Battery Company, Inc.), 5,789,108 (PolyPlus Battery Company, Inc.), and 5,814,420 (PolyPlus Battery Company, Inc.) describe that an organic liquid electrolyte is selected from sulfolane

compounds, dimethyl sulfone compounds, dialkyl carbonate compounds, tetrahydrofuran compounds, propylene carbonate compounds, ethylene carbonate compounds, dimethyl carbonate compounds, butyrolactone compounds, N,N-methylpyrrolidone, tetramethylurea compounds, glymes compounds, ether compounds, crown ether compounds, dimethoxyethane compounds, dioxolane compounds and combinations thereof. In addition, U.S. Patent No. 5,814,420 (PolyPlus Battery Company, Inc.) describes a liquid state ionic conductor of a positive electrode that includes at least one of sulfolane, dimethyl sulfone, a dialkyl carbonate, tetrahydrofuran, propylene carbonate, ethylene carbonate, dimethyl carbonate, butyrolactone, N-methylpyrrolidone, tetramethylurea, glymes, ether, a crown ether, dimethoxyethane and dioxolane.

**[0006]** U.S. Patent No. 6,030,720 (PolyPlus Battery Company) describes a liquid electrolyte solvent that includes a main solvent having the general formula  $R_1(CH_2CH_2O)_nR_2$ , where  $n$  ranges between 2 and 10,  $R_1$  and  $R_2$  are different or identical groups selected from alkyl, alkoxy, substituted alkyl, or substituted alkoxy groups, and also describes a liquid electrolyte solvent including a solvent having at least one of a crown ether, cryptand, and a donor solvent. Some electrolyte solvents include donor or acceptor solvents in addition to the above compound with an ethoxy repeating unit. The donor solvent is at least one of hexamethylphosphoric triamide, pyridine, N,N-diethylacetamide, N,N-diethylformamide, dimethylsulfoxide, tetramethylurea, N,N-dimethylacetamide, N,N-dimethylformamide, tributylphosphate, trimethylphosphate, N,N,N',N'-tetraethylsulfamide, tetramethylenediamine, tetramethylpropylenediamine, or pentamethyldiethylenetriamine.

**[0007]** WO 99/33131 (Moltech Company) describes an electrolyte that comprises one or more electrolyte solvent selected from N-methylacetamide, acetonitrile, carbonate, sulfolane, sulfone, substituted pyrrolidone, dioxolane, glyme or siloxane.

**[0008]** The battery performances (e.g., capacity and rate capability) depend greatly on the composition of the electrolyte solvents. However, the specific composition or developing strategy of an optimal electrolyte (making a optimal electrolyte) which are necessary for the development of lithium-sulfur batteries of good performance, are not mentioned in the prior art.

## SUMMARY OF THE INVENTION

**[0009]** It is an object of the present invention to provide a lithium-sulfur battery having a high capacity and a good rate capability through methods of making an optimal electrolyte.

[0010] Additional objects and advantages of the invention will be set forth in part in the description which follows and, in part, will be obvious from the description, or may be learned by practice of the invention.

[0011] In order to realize the above and other objects, a lithium-sulfur battery according to an embodiment of the present invention includes a negative electrode, a positive electrode and an electrolyte, where the negative electrode includes active materials selected from materials in which lithium intercalation reversibly occurs, lithium alloy, and lithium metal, the positive electrode includes sulfur-based compounds for an active material, and an electrically conductive material, the sulfur-based compounds include at least one of elemental sulfur, and organosulfur compounds, the electrolyte includes the mixed organic solvents, which include at least two groups selected from a weak polar solvent group, a strong polar solvent group, and a lithium protection solvent group, ones of the electrolytes include at least one or more solvents selected from the same group, and the electrolyte includes one or more electrolyte salts.

[0012] According to another embodiment of the present invention, the positive electrode includes at least one additive selected from transition metals, Group IIIA elements, Group IVA elements, sulfur compounds thereof, or alloys thereof.

[0013] According to a further embodiment of the present invention, when the lithium-sulfur battery is discharged, polysulfides ( $S_n^{-1}$ ,  $S_n^{-2}$ , where,  $n \geq 2$ ) and sulfide ( $S^{-2}$ ) are formed by a reduction of sulfur in the positive electrode.

[0014] According to an aspect of the present invention, the polysulfides are known to exist in a dissolved state in the electrolyte and the sulfide in a precipitated state, the solubility of elemental sulfur to the mixed organic solvents is preferably more than or equal to 0.5 mM, and in order to prepare a battery with high capacity, the atomic sulfur concentration of polysulfide ( $S_n^{-1}$ ,  $S_n^{-2}$ , where,  $n \geq 2$ ) produced in a fully discharged state is preferably at least 5 M.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0015] These and other objects and advantages of the invention will become apparent and more readily appreciated from the following description of the preferred embodiments, taken in conjunction with the accompanying drawing of which

FIG. 1 shows discharge curves of lithium-sulfur battery fabricated by using electrolytes

of Example 1, and Comparative examples 1 and 3.

## DETAILED DESCRIPTION OF THE INVENTION

**[0016]** Reference will now be made in detail to the present preferred embodiments of the present invention, examples of which are illustrated in the accompanying drawing, wherein like reference numerals refer to the like elements throughout. The embodiments are described below in order to explain the present invention by referring to the figure.

**[0017]** The present invention provides a lithium-sulfur battery having a high capacity and a good rate capability. One of important factors related to the capacity of the lithium-sulfur battery is sulfur utilization, which depends dramatically on electrolytes. Therefore, the optimization of the composition of the electrolyte solvents is an important factor for the development of lithium-sulfur batteries having a high capacity. The rate capability of lithium-sulfur battery also depends greatly on the composition of the electrolyte solvents since the rate of the electrochemical reaction is directly related to the electrolyte solvents.

**[0018]** Levillain et al., On The Understanding Of The Reduction Of Sulfur ( $S_8$ ) In Dimethylformamide (DMF), J. Electroanal. Chem., Vol. 420, pp 167-177, (1997), F. Gaillard et al., Polysulfides In Dimethylformamide: Only The Radical Anions  $S_3^{\cdot-}$  And  $S_4^{\cdot-}$  Are Reducible, J. Electroanal. Chem., Vol. 432, pp 129-138, (1997), E. Levillain et al., Polysulfides In Dimethylformamide: Only The Redox Couples  $S_N^{\cdot-}/S_N^{2-}$  Are Involved, J. Electroanal. Chem., Vol. 440, pp 243-250, (1997) describe in detail that the electrochemical reaction of sulfur consists of various electrode reactions and various coupled chemical reactions. Poor reversibility and slow rate constant of the coupled chemical reaction lead to low sulfur utilization and poor rate capability since the chemical reactions are related directly to the electrode reactions.

**[0019]** Generally, oxidation numbers of sulfur in the polysulfides ( $S_n^{-1}$ ,  $S_n^{-2}$ , where,  $n \geq 1$ ) which are reduction products of sulfur are more than 0 or less than -2. The terminology "oxidation number of sulfur", as used herein, is defined as the value of the ratio of charge-to-sulfur-chain length. The polysulfides where an oxidation number of sulfur is near 0 are dissolved in a weak polar solvent, while the polysulfides where oxidation numbers of sulfur are less than or equal to -1 are dissolved in a strong polar solvent. Therefore, in order to dissolve polysulfide with various oxidation numbers, it is necessary to use mixed solvents including a weak polar solvent and a strong polar solvent as an electrolyte solvent.

**[0020]** The mixed organic solvents of the electrolyte of the present invention include at least two groups selected from a weak polar solvent group, a strong polar solvent group, and a lithium protection solvent group. Some electrolytes include at least one or more solvents selected from the same group.

**[0021]** The terminology "weak polar solvent," as used herein, is defined as a solvent which is capable of dissolving elemental sulfur and has a dielectric coefficient of less than 15. The weak polar solvent is selected from an aryl compound, cyclic ether compound, noncyclic ether compound, or a noncyclic carbonate compound.

**[0022]** The terminology "strong polar solvent," as used herein, is defined as a solvent which is capable of dissolving lithium polysulfide and has a dielectric coefficient of more than 15. The strong polar solvent is selected from a cyclic carbonate compound, a sulfoxide compound, a lactone compound, a ketone compound, an ester compound, a sulfate compound, or a sulfite compound.

**[0023]** The terminology "lithium protection solvent," as used herein, is defined as a solvent which form a good protective layer, (i.e. a stable solid-electrolyte interface (SEI) layer), on a lithium surface, and shows a good cyclic efficiency. The lithium protection solvent is selected from a saturated ether compound, an unsaturated ether compound, or a heterocyclic compound including N, O, and S.

**[0024]** Examples of the weak polar solvents include xylene, dimethoxyethane, 2-methyltetrahydrofuran, diethyl carbonate, dimethyl carbonate, toluene, dimethyl ether, diethyl ether, diglyme or tetraglyme.

**[0025]** Examples of the strong polar solvents include hexamethyl phosphoric triamide,  $\gamma$ -butyrolactone, acetonitrile, ethylene carbonate, propylene carbonate, N-methyl pyrrolidone, 3-methyl-2-oxazolidone, dimethyl formamide, sulfolane, dimethyl acetamide, dimethyl sulfoxide, dimethyl sulfate, ethylene glycol diacetate, dimethyl sulfite, or ethylene glycol sulfite.

**[0026]** Examples of the lithium protection solvents include tetrahydrofuran, ethylene oxide, 1,3-dioxolane, 3,5-dimethylisoxazole, 2,5-dimethyl furane, furane, 2-methyl furane, 1,4-oxane and 4-methyldioxolane.

**[0027]** Examples of electrolyte salts which are optional for the battery according to the

present invention include lithium trifluoromethane sulfonimide, lithium triflate, lithium perchlorate,  $\text{LiPF}_6$  or  $\text{LiBF}_4$ , tetraalkylammonium salts, (e.g. tetrabutylammonium tetafuloroborate ( $\text{TBABF}_4$ )), liquid state salts at room temprature, (e.g. imidazolium salt such as 1-ethyl-3-methylimidazolium Bis-(perfluoroethyl sulfonyl) imide (EMIBeti)), or combinations thereof.

**[0028]** The positive electrode includes sulfur-based compounds for a positive active material, which include at least one of elemental sulfur, and organosulfur compounds. The positive electrode may optionally include at least one additive selected from transition metals, Group IIIA elements, Group IVA elements, sulfur compounds thereof, or alloys thereof. The transition metal includes Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, Ta, W, Re, Os, Ir, Pt, Au and Hg. The Group IIIA elements include Al, Ga, In and Tl. The Group IVA elements include Si, Ge, Sn and Pb.

**[0029]** The positive electrode includes electrically conductive materials that facilitate the movement of electrons within the positive electrode with sulfur-based compound or optionally include additives. Examples of the conductive material are not limited to these but include a conductive carbon material such as graphite, carbon black, a conductive polymer such as polyaniline, polythiophene, polyacetylene, or polypyrrol, or a combination thereof.

**[0030]** A binder may be added to enhance the mechanical integrity of the positive electrode, to improve mechanical and electrical contact at the solid-solid interface and/or the solid/liquid interface, to increase electronic and/or ionic conduction throughout the positive electrode, and still further, to enhance the electrochemical redox reactions. Examples of the binder include poly(vinyl acetate), poly vinyl alcohol, polyethylene oxide, polyvinyl pyrrolidone, alkylated polyethylene oxide, cross linked polyethylene oxide, polyvinyl ether, poly(methyl methacrylate), polyvinylidene fluoride, copolymer of polyhexafluoropropylene and polyvinylidene fluoride (sold under the name Kynar®), poly(ethyl acrylate), polytetrafluoro ethylene, polyvinyl chloride, polyacrylonitrile, polyvinylpyridine, polystyrene, derivatives thereof, blends thereof, and copolymers thereof.

**[0031]** A method of preparing a positive electrode will be illustrated in more detail. A binder is dissolved in a solvent and a conductive material is dispersed therein to obtain a dispersion solution. Any solvent may be used as long as it is capable of homogeneously dispersing a sulfur-based compound, the binder and the conductive material. Useful solvents include

acetonitrile, methanol, ethanol, tetrahydrofurane, water, isopropyl alcohol, and dimethyl formamide. Then, a sulfur-based compound and, optionally, an additive, are homogeneously dispersed in the dispersion solution to prepare a positive electrode slurry. The slurry is coated on a current collector and the coated collector is dried to form a positive electrode. The current collector is not limited to, but is preferably made of a conductive material such as stainless steel, aluminum, copper or titanium. It is more preferable to use a carbon-coated aluminum current collector. The carbon-coated aluminum current collector has excellent adhesive properties for the coated layer including positive materials, exhibits a lower contact resistance, and inhibits corrosion by polysulfide as compared with a bare aluminum current collector.

**[0032]** The negative electrode includes a negative active material selected from materials in which lithium intercalation reversibly occurs, lithium alloy, or a lithium metal. The lithium alloy includes a lithium/ aluminum alloy, or a lithium/ tin alloy.

**[0033]** The materials in which lithium intercalation reversibly occurs are carbon-based compounds. Any carbon materials may be used as long as it is capable of intercalating and deintercalating lithium ions. Examples of the carbon material include crystalline carbon, amorphous carbon, or a mixture thereof.

**[0034]** Porosity of the positive electrode is a very important factor in determining the amount of impregnation of an electrolyte. If porosity is very low, discharging occurs locally, which causes a high concentration of lithium polysulfide and makes precipitation easily, which decreases the sulfur utilization. Meanwhile, if the porosity is very high, a slurry density becomes low so that it is difficult to prepare a battery with a high capacity. Preferably, the porosity of the positive electrode is at least 5% of the volume of the total positive electrode, more preferably it is at least 10%, and most preferably, it is 15 to 65%.

**[0035]** Upon discharge of the lithium-sulfur battery of the present invention, polysulfides ( $S_n^{-1}$ ,  $S_n^{-2}$ , wherein,  $n \geq 2$ ) or sulfide are formed by a reduction of the sulfur in the positive electrode. Generally, the polysulfides are known to exist in a dissolved state in the electrolyte and sulfide in a precipitated state. The solubility of elemental sulfur to the mixed organic solvent is preferably 0.5 mM or more. In order to prepare a battery with high capacity, the concentration of atomic sulfur of polysulfide ( $S_n^{-1}$ ,  $S_n^{-2}$ , where,  $n \geq 2$ ) produced in fully discharged state is preferably at least 5 M.

**[0036]** Hereinafter, the present invention will be explained in detail with reference to

examples. These examples, however, should not in any sense be interpreted as limiting the scope of the present invention.

#### Example 1

[0037] 20 % (percentage by weight) polyvinyl pyrrolidone as a binder and 20 % carbon black as a conductive material were added to a dimethylformamide solvent followed by the addition of 60 % elemental sulfur to prepare a slurry. The slurry was coated on a carbon-coated Al current collector. Then, the slurry-coated current collector was dried. The positive electrode and the vacuum dried separator were transferred into a glove box. The electrolyte of 1M  $\text{LiSO}_3\text{CF}_3$  in dimethoxyethane/sulfolane/1,3-dioxolane (3:1:1 volume ratio) was placed on the positive electrode followed by placement of the separator. Traces of the electrolyte were then added on the separator. A lithium metal electrode as a negative electrode was placed on the separator, and then the lithium-sulfur cell was fabricated in a conventional manner.

#### Example 2

[0038] A cell was fabricated by the same procedure as described in Example 1 except that an electrolyte of 1 M  $\text{LiSO}_3\text{CF}_3$  in dimethoxyethane/sulfolane/1,3-dioxolane (2:2:1 volume ratio) was used.

#### Example 3

[0039] A cell was fabricated by the same procedure as described in Example 1 except that an electrolyte of 1 M  $\text{LiSO}_3\text{CF}_3$  in dimethoxyethane/sulfolane/dimethylsulfoxide/1,3-dioxolane (20:16:4:10 volume ratio) was used.

#### Example 4

[0040] A cell was fabricated by the same procedure as described in Example 1 except that an electrolyte of 1 M  $\text{LiSO}_3\text{CF}_3$  in dimethoxyethane/2-methyltetrahydrofuran/sulfolane/1,3-dioxolane (16:4:20:10 volume ratio) was used.

#### Example 5

[0041] A cell was fabricated by the same procedure as described in Example 1 except that an electrolyte of 1 M  $\text{LiSO}_3\text{CF}_3$  in dimethoxyethane/3,5-dimethylisoxazole/sulfolane/1,3-dioxolane (4:1:4:1 volume ratio) was used.



## Example 6

**[0042]** A cell was fabricated by the same procedure as described in Example 1 except that an electrolyte of 1 M  $\text{LiSO}_3\text{CF}_3$  in 3,5-dimethylisoxazole/sulfolane/1,3-dioxolane (1:2:2 volume ratio) was used.

## Example 7

**[0043]** A cell was fabricated by the same procedure as described in Example 1 except that an electrolyte of 1 M  $\text{LiSO}_3\text{CF}_3$  in dimethoxyethane/diglyme/sulfolane/1,3-dioxolane (2:2:1:5 volume ratio) was used, and a 3 % nickel powder based on the weight of the sulfur was further added to the slurry.

## Comparative Example 1

**[0044]** A cell was fabricated by the same procedure as described in Example 1 except that an electrolyte of 1 M  $\text{LiSO}_3\text{CF}_3$  in dimethoxyethane was used.

## Comparative Example 2

**[0045]** A cell was fabricated by the same procedure as described in Example 1 except that an electrolyte of 1 M  $\text{LiSO}_3\text{CF}_3$  in dimethoxyethane/xylene (4:1 volume ratio) was used.

## Comparative Example 3

**[0046]** A cell was fabricated by the same procedure as described in Example 1 except that an electrolyte of 1 M  $\text{LiSO}_3\text{CF}_3$  in dimethoxyethane/1,3-dioxolane (4:1 volume ratio) was used.

## Comparative Example 4

**[0047]** A cell was fabricated by the same procedure as described in Example 1 except that an electrolyte of 1 M  $\text{LiSO}_3\text{CF}_3$  in dimethoxyethane/diglyme/sulfolane/1,3-dioxolane (2:2:1:5 volume ratio) was used.

**[0048]** Sulfur utilization of the cells according to Examples 1 to 7 and Comparative examples 1 to 4 was evaluated at ambient temperature. Discharge current density was set to 0.185  $\text{mA}/\text{cm}^2$  and charge current density was set to 0.37  $\text{mA}/\text{cm}^2$ . Discharge cut-off voltage was set to 1.5 V and charge capacity was set to 55% of theoretical capacity. In addition, sulfur utilization of Example 1 and Comparative example 3 at discharge current density of 0.925  $\text{mA}/\text{cm}^2$  and 1.85  $\text{mA}/\text{cm}^2$  were evaluated respectively. The result of sulfur utilization is

presented in Table 1. The sulfur utilization is defined as the percent values of observed capacity to the theoretical capacity, *i.e.*, 1675 mAh/g.

TABLE 1

	Solvents of electrolyte	Discharging current density (mA/cm <sup>2</sup> )	Sulfur utilization (%)
Example 1	dimethoxyethane/sulfolane/1,3-dioxolane (3:1:1)	0.185	66
Example 1	dimethoxyethane/sulfolane/1,3-dioxolane (3:1:1)	0.925	58
Example 1	dimethoxyethane/sulfolane/1,3-dioxolane (3:1:1)	1.85	49
Example 2	dimethoxyethane/sulfolane/1,3-dioxolane (2:2:1)	0.185	66
Example 3	dimethoxyethane/sulfolane/ dimethylsulfoxide/1,3-dioxolane (20:16:4:10)	0.185	68
Example 4	dimethoxyethane/2-methyltetrahydrofuran/sulfolane/1,3-dioxolane (16:4:20:10)	0.185	65
Example 5	dimethoxyethane/3,5-dimethylisoxazole/sulfolane/1,3-dioxolane (4:1:4:1)	0.185	59
Example 6	3,5-dimethylisoxazole/sulfolane/1,3-dioxolane (1:2:2)	0.185	59
Example 7	dimethoxyethane/diglyme/sulfolane/1,3-dioxolane (2:2:1:5)	0.185	61
Comparative Example 1	Dimethoxyethane	0.185	34
Comparative Example 2	dimethoxyethane/xylene(4:1)	0.185	12

	Solvents of electrolyte	Discharging current density (mA/cm <sup>2</sup> )	Sulfur utilization (%)
Comparative Example 3	dimethoxyethane/1,3-dioxolane (4:1)	0.185	56
Comparative Example 3	dimethoxyethane/1,3-dioxolane (4:1)	0.925	43
Comparative Example 3	dimethoxyethane/1,3-dioxolane (4:1)	1.85	33
Comparative Example 4	dimethoxyethane/diglyme/sulfolane/1,3-dioxolane (2:2:1:5)	0.185	53

**[0049]** Sulfur utilization depends greatly on the composition of the electrolyte as shown in Table 1. As evident from Table 1, the Comparative examples 1 and 2 show that a solvent of a weak polar solvent group or two solvents of a weak solvent group have poor sulfur utilization compared with others. Meanwhile, the cells according to Examples 1 to 6 using at least two solvents selected from a weak polar solvent group, a strong solvent group, and a lithium protection solvent group, have excellent sulfur utilization. Especially, when the discharging current density was increased to 1.85mA/cm<sup>2</sup>, the sulfur utilization of Example 1 was higher than that of Comparative examples 1 or 2 at 0.185mA/cm<sup>2</sup>.

**[0050]** Comparing Example 1 with Comparative example 3, the sulfur utilization of the mixed organic solvent including a weak polar solvent, a strong polar solvent, and a lithium protection solvent (Example 1), was higher than that of the mixed organic solvent including a weak polar solvent and lithium protection solvent (Comparative example 3). In addition, comparing Example 7 with Comparative example 4, the improvement of the sulfur utilization in the cells with Ni (Example 7) was observed.

**[0051]** Fig. 1 shows discharge curves of the cells according to Example 1, and Comparative examples 1 and 3 at 0.185mA/cm<sup>2</sup>. It shows that the cell of Example 1 including a weak polar solvent, a strong polar solvent, and a lithium protection solvent has the highest discharging voltage, while the cell of Comparative example 1 including only a weak polar solvent has the lowest discharging voltage.

**[0052]** While the present invention has been described in detail with reference to the preferred embodiments, those skilled in the art will appreciate that various modifications and substitutions can be made thereto without departing from the spirit and scope of the present invention as set forth in the appended claims and their equivalents.